



TITLE:

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and Hydrogen (Commemoration Issue  
Dedicated to Professor Yoshimasa Takezaki  
on the Occasion of his Retirement)

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## Kinetic Studies on the Carbonylation of Amine Using Compressed Carbon Dioxide and Hydrogen

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N,N-Dimethylformamide (DMF) was synthesized from dimethylamine (DMA), carbon dioxide and hydrogen catalyzed by tris (triphenylphosphine) rhodium (I) chloride in Methyl Cellosolve-benzene mixed solvent. The effect of the following variables on the rate was examined kinetically: initial concentrations of catalyst and DMA, partial pressures of carbon dioxide and hydrogen, and temperature. The rate of DMF formation has been found as:

$$[\text{DMF}] = [\text{DMA}]_0 \left\{ 1 - \exp \left[ - \frac{C_1 [\text{CO}_2] [\text{H}_2] [\text{Cat}]_0}{(1 + C_2 [\text{CO}_2]) (1 + C_3 [\text{H}_2])} \right] t \right\}$$

where  $C_1$ ,  $C_2$  and  $C_3$  are constants.

A mechanism is proposed involving an assumed hydrocarbamatorrhodium complex as the reaction intermediate:



KEY WORDS: Dimethylamine/ Synthesis of N,N-Dimethylformamide/ High pressure/ Catalytic reaction/ Kinetics and mechanism/

### INTRODUCTION

As carbon dioxide incessantly released into the atmosphere is thought to be an abundant resource for chemical industry, its reactions with organic compounds has recently been much interested. Because of the high stability of this compound, little progress has ever been made and it seems that, to overcome this hurdle, more powerful catalysts should be supplied especially from the field of organometallic chemistry.

Aside from the use of organic or inorganic strong bases as carriers of carbon dioxide,<sup>1)</sup> an important series of reactions was first carried out by Adkins *et al.*,<sup>2)</sup> who claimed that carbon dioxide was reduced by hydrogen with a transition metal catalyst to formic acid, which itself in the presence of amine formed formate or formamide depending on the reaction temperature:



Kohlne *et al.*<sup>3)</sup> prepared N,N-dimethylformamide (DMF) from  $\text{CO}_2$ ,  $\text{H}_2$  and dimethylamine (DMA) under mild conditions by the use of various transition metal complexes

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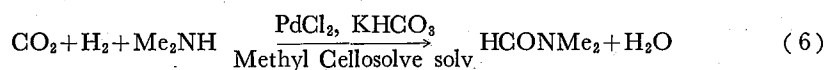
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as catalysts, but the yield of DMF was still low [Eq. (4)].

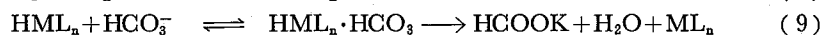


Employing deuterium instead of hydrogen, at least in the case of the iridium complex, Kohlne *et al.* proved the participation of the hydride in the DMF formation reaction, but further investigation on the reaction mechanism was not made.<sup>3)</sup>

Independently we found that the formate could be obtained from  $\text{CO}_2$ ,  $\text{H}_2$  and potassium hydrocarbonate with palladium chloride as catalyst,<sup>4)</sup> and that in the presence of DMA, DMF was formed in high yield<sup>5)</sup>:



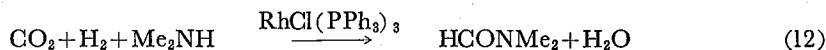
On the basis of further studies on mechanism, we have proposed the following mechanism for the reaction (5), that is, the reaction does not proceed *via* the interaction of metal hydride and  $\text{CO}_2$  but *via* that of metal hydride and hydrocarbonate ion:



Contrary to this, the abnormal insertion mechanism, as was called by Volpin first,<sup>6)</sup> of  $\text{CO}_2$  into the metal-hydrogen bond is also possible since some formate-transition metal complexes such as  $\text{HCOORu}(\text{PPh}_3)_4$  has been prepared and isolated<sup>7)</sup>:



As no other detailed studies have been found, we will report in this paper the results of the kinetic studies on the formation of DMF from DMA,  $\text{CO}_2$  and  $\text{H}_2$ , by the use of tris(triphenylphosphine)rhodium(I) chloride as catalyst in the Methyl Cellosolve-benzene mixed solvent:



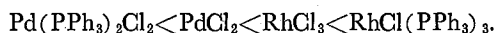
## RESULTS AND DISCUSSION

*Preliminary investigation.* In order to get rough features and favorable conditions of the reaction, preliminary experiments were carried out, the results being given in Table I. The gas chromatography proved the absence of the side reaction except Run 7 (dimethyl sulfoxide solvent). It seems that water does not affect the reaction so much as in the reaction of formic acid synthesis reported by Inoue *et al.*<sup>8)</sup> (Run 1 and 2). The activity of the catalysts for the present reaction is parallel to that in the general hydrogenation of olefins (Run 1 to 5):

Table I. Preliminary survey of the reaction conditions

Run	Solvent	Reaction conditions <sup>a)</sup>			time (h)	temp (°C)	Results yield <sup>b)</sup> (mol %)
		(ml)	Catalyst	(mmol)			
1	MC <sup>c)</sup> : H <sub>2</sub> O	10: 0.2	PdCl <sub>2</sub>	0.52	5	170	33
2	MC	10	PdCl <sub>2</sub>	0.52	5	170	39
3	MC	10	PdCl <sub>2</sub> + PPh <sub>3</sub>	0.48 0.59	5	170	6.0
4	MC: H <sub>2</sub> O	10: 1	RhCl <sub>3</sub> 3H <sub>2</sub> O	0.21	9	170	34
5	MC: H <sub>2</sub> O	10: 1	RhCl <sub>3</sub> 3H <sub>2</sub> O + PPh <sub>2</sub>	0.22 0.58	9	170	41
6	MC	10	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	0.18	5	150	65
7	DMSO <sup>d)</sup>	10	PhCl(PPh <sub>3</sub> ) <sub>3</sub>	0.17	5	150	69
8	Benzene	10	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	0.071	5	150	8.3
9	MC	10	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	0.17	5	105	48
10	MC: Benzene	5: 5	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	0.13	2.5	175	27
11	MC: Benzene	5: 5	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	0.11	2.5	105	21
12	MC: Benzene	7: 7	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	0.053	5	r. t	0

a) charged DMA=10 mmol, P<sub>CO<sub>2</sub></sub>=40 kg/cm<sup>2</sup> (at r. t), P<sub>H<sub>2</sub></sub>=80 kg/cm<sup>2</sup> (at r. t), b) based on charged DMA, c) Methyl Cellosolve, d) dimethyl sulfoxide.



In the case of rhodium complexes, the solutions were homogeneous while the palladium complexes were reduced to the metal precipitated at the end of the reaction. In Methyl Cellosolve which is usually a good solvent for the synthetic reaction of amide from amine,<sup>5,9)</sup> the yield is much higher than in the nonpolar solvent, benzene (Run 6 and 8). In dimethyl sulfoxide the yield is high, but some complications occurred due to the decomposition of the solvent (Run 7). As it is desirable to make an induction period as short as possible, the mixed solvent of Methyl Cellosolve and benzene was chosen for the kinetic studies. The temperature range from 100°C to 150°C is preferable to the reaction, as the catalyst was found to be spoiled at higher temperature.

Since it is reported that RhCl(PPh<sub>3</sub>)<sub>3</sub> dissolved in a solvent reacts easily with oxygen, and that the oxidated species is more active for the hydrogenation reaction of olefin,<sup>10)</sup> we carried out experiments to compare the reaction in the air-free solvent with that in the non-air-free solvent and found that a small amount of air dissolved in the solvent did not affect the rate of the reaction (Run 10 in Table IV).

As needed later for analyzing kinetic data, the solubilities of CO<sub>2</sub> and H<sub>2</sub> in Methyl Cellosolve-benzene mixed solvent (2 to 1 in volume ratio) were measured at 90°C, 105°C and 120°C. Henry's law fails almost usually when gas concentration in liquid is high,<sup>11)</sup> but fortunately this law holds for the present case as seen in Fig. 1, in spite of the high solubility of CO<sub>2</sub> in the mixed solvent. The measured values of the solubility constants are listed in Table II. It has been also confirmed that the additivity rule holds between the solubilities of CO<sub>2</sub> and H<sub>2</sub> in good approximation. The solubilities of CO<sub>2</sub> at 100

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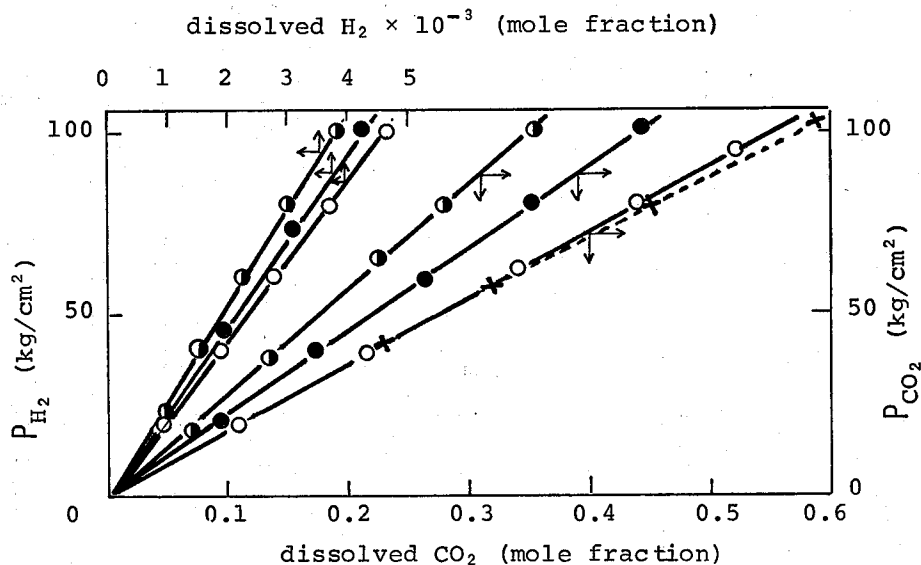


Fig. 1. Solubility of CO<sub>2</sub> and H<sub>2</sub> in benzene and benzene-Methyl Cellosolve mixed solvent (Volume ratio=1/2).

---x---: in benzene at 105°C, ○: 90°C, ●: 105°C, ◐: 110°C, in MC.

Table II. Solubility constants of CO<sub>2</sub> and H<sub>2</sub> in MC-Benzene mixed solvent (Volume ratio 2 : 1)

temp (°C)	H <sub>CO<sub>2</sub></sub> (kg/cm <sup>2</sup> )/ (mole fraction)	H <sub>H<sub>2</sub></sub> (kg/cm <sup>2</sup> )/ (mole fraction)
90	0.184×10 <sup>3</sup>	2.19×10 <sup>3</sup>
105	0.230×10 <sup>3</sup>	2.34×10 <sup>3</sup>
120	0.286×10 <sup>3</sup>	2.63×10 <sup>3</sup>

Table III. Solubility of CO<sub>2</sub> in various solvents (100 kg/cm<sup>2</sup>, 105°C)

Solvent	[CO <sub>2</sub> ] <sub>d</sub> <sup>a</sup> (mole fraction)
Benzene	0.85
Tetrahydrofuran	0.55
Methyl Cellosolve	0.36
1-Propanol	0.30
Ethylene Glycol	0.05

a) [CO<sub>2</sub>]<sub>d</sub> denotes the concentration of CO<sub>2</sub> dissolved in the solvent.

kg/cm<sup>2</sup> and at 150°C in several solvents were also measured (Table III); the results are in decreasing order:

benzene>tetrahydrofuran>Methyl Cellosolve>n-propanol»ethylene glycol.

The effect of the stirring speed was also examined to assure that the diffusion of both gases did not affect the rate of the reaction at the stirring speed greater than 1000 rpm. Thus, all the kinetic experiments were carried out at 1200 rpm.

**Kinetic results.** Kinetic examinations were done in the MC-benzene (2:1) mixed solvent within the limit of temperature where Eq. (14) holds, or the rate being of the first order as to the substrate concentration. The rate constants,  $k_{obs}$ 's obtained from Eq. (14), are listed in Table IV. The relation between  $k_{obs}$  and catalyst concentration, hydrogen and carbon dioxide pressure have been found as the empirical expressions

Table IV. Values of  $k_{obs}$  at various Conditions<sup>a)</sup>

		conditions						Results		
	No	DMA <sup>b)</sup> (mmol)	Solvent (volume ratio)	Temp (°C)	Cat <sup>b)</sup>	$P_{CO_2}$ (kg/cm <sup>2</sup> )	$P_{H_2}$ (kg/cm <sup>2</sup> )	$k_{obs}^c)$ (hr <sup>-1</sup> )	$t_o$ (min)	Yield <sup>d)</sup> (mol %)
Solvent Effect	1	50	Benzene	105	0.325mmol	100	100	—	small	55
	2	50	Benzene <sup>e)</sup>	105	0.325mmol	100	100	—	small	19
	3	50	MC <sup>d)</sup>	105	0.325mmol	100	100	0.15	30	48
	4	50	MG <sup>d)</sup>	105	0.325mmol	100	100	≥0.15	140	35
	5	50	n-Propanol	105	0.325mmol	100	100	0.088	30	34
	6	50	THF <sup>f)</sup>	105	0.325mmol	100	100	—	small	20
	7	50	MeOH-Benzene (2:1)	105	0.325mmol	100	100	0.040	20	18
	8	50	MC-Benzene (1:2)	105	0.325mmol	100	100	0.20	5	58
	9	50	MC-Benzene (2:1)	105	0.325mmol	100	100	0.18	20	56
Temperature Effect	10 <sup>g)</sup>	50	“	105	0.325mmol	100	100	0.18	20	56
	11	50	“	135	0.542mmol	100	100	—	small	80
	12	50	“	120	0.542mmol	100	100	0.33	2	76
	13	50	“	110	0.542mmol	100	100	0.24	5	68
	14	50	“	105	0.542mmol	100	100	0.20	20	61
	15	50	“	100	0.542mmol	100	100	0.15	40	48
	16	50	“	90	0.542mmol	100	100	0.11	—	—
	17 <sup>h)</sup>	50	“	105	0.542mmol	100	100	0.20	20	60
	18 <sup>i)</sup>	50	“	105	0.325mmol	100	100	0.18	20	56
Catalyst Concentration Effect	19	100	“	105	0.325mmol	100	100	0.18	30	53
	20	50	“	105	0.146mmol	100	100	0.078	20	
	21	50	“	105	0.163mmol	100	100	0.11	20	
	22	50	“	105	0.216mmol	100	100	0.14	20	
	23	50	“	105	0.407mmol	100	100	0.18	20	
	24	50	“	105	0.541mmol	100	100	0.20	20	
	25	50	“	105	1.085mmol	100	100	0.20	20	
	26	50	“	105	2.165mmol	100	100	0.23	20	
	27	50	“	105	0.140 × 10 <sup>-3</sup> (mole fraction)	10	100	0.048	50	
CO <sub>2</sub> Pressure Effect	28	50	“	105	“	20	100	0.080	45	
	29	50	“	105	“	40	100	0.12	23	
	30	50	“	105	“	70	100	0.16	20	
	31	50	“	105	“	120	100	0.21	5	
	32	50	“	105	“	140	100	0.21	5	
	33	50	“	90	“	20	100	0.031	80	
	34	50	“	90	“	40	100	0.050	40	
	35	50	“	90	“	100	100	0.083	20	
	36	50	“	105	“	100	23	0.065	20	
H <sub>2</sub> Pressure Effect	37	50	“	105	“	100	40	0.11	20	
	38	50	“	105	“	100	70	0.15	20	
	39	50	“	105	“	100	120	0.205	20	
	40	50	“	90	“	100	20	0.029	20	
	41	50	“	90	“	100	40	0.052	20	
	42	50	“	90	“	100	70	0.066	20	

a) Stirring speed 1200 rpm. b) The charged DMA and RhCl(PPh<sub>3</sub>)<sub>3</sub> are given in mmol, but the values of their initial concentrations vary slightly according to the solubility of CO<sub>2</sub> at different temperature. From No 27 (Effect of CO<sub>2</sub> and H<sub>2</sub> pressure), the catalyst was charged in such an amount that its initial concentration remains the same at various temperature and CO<sub>2</sub> pressure. c) In benzene or at high temperature the values of  $k_{obs}$  cannot be found. d) At 5 hrs and based on charged DMA. e) Before H<sub>2</sub> was added, the solution had been stirred for 2 hrs under 100 kg/cm<sup>2</sup> of CO<sub>2</sub> pressure. f) MC=Methyl Cellosolve, EG=ethylene glycol, THF=tetrahydrofuran. g) The reaction was carried in the air-free solvent. h) H<sub>2</sub>O=55.6 mmol was added. i) DMF=39 mmol was added. j) Effect of substrate and product initial concentration.

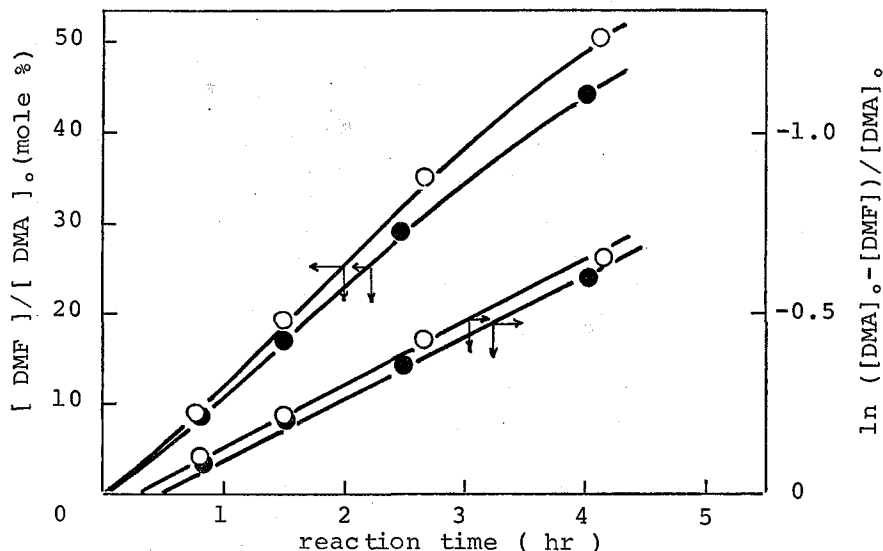


Fig. 2. Effect of substrate concentration.

solvent: MC-benzene (2 : 1),  $[\text{Cat}]_0 = 0.140 \times 10^{-3}$  mol fraction,  $\text{temp} = 105^\circ\text{C}$ ,  $P_{\text{CO}_2} = 100 \text{ kg/cm}^2$ ,  $P_{\text{H}_2} = 100 \text{ kg/cm}^2$ , ○ :  $[\text{DMA}]_0 = 0.0208$  mole fraction, ● :  $[\text{DMA}]_0 = 0.0416$  mole fraction.

(15), (16) and (17).

(a) *Substrate concentration*: The relations of yield against time are plotted at two different initial concentrations of substrate (Fig. 2). We note here that these two curves are almost parallel with only small difference depending on the induction period, and the rate seems to be of first order as regards the concentration of the substrate. In fact, the plot of  $\ln ([\text{DMA}]_0 - [\text{DMF}])/[\text{DMA}]_0$  against time is linear (Fig. 2) and, though the two induction periods are different with each other, the slopes obtained are the same. So we can write the experimental expression as:

$$\ln \frac{[\text{DMA}]_0 - [\text{DMF}]}{[\text{DMA}]_0} = -k_{\text{obs}}(t - t_0), \quad (14)$$

where the induction period  $t_0$  is defined as the intercept of the extrapolated straight line of  $\ln ([\text{DMA}]_0 - [\text{DMF}])/[\text{DMA}]_0$  against time plot on the time axis. This linear plot of the substrate concentration is quite important since it gives the induction period  $t_0$  and also the criterion for the activity of catalyst remaining unchanged during the reaction period. On the other hand, reuse of the catalyst was attempted as described below. After a solution of 50 mmol of DMA and 0.325 mmol of  $\text{RhCl}(\text{PPh}_3)_3$  in the mixed solvent was stirred for 5 hr under 100 kg/cm<sup>2</sup> of  $\text{CO}_2$  and 100 kg/cm<sup>2</sup> of  $\text{H}_2$  at 105°C, another 50 mmol of DMA was added to this and the reaction was continued for further 5 hr. The yield of DMF formed in both cases were almost the same, so that we can conclude in 10 hr at least, no deactivation of catalyst occurred at this temperature, while the catalyst was almost spoiled at 170°C.

(b) *Solvent*: The rate is higher in benzene chosen as the typical nonpolar solvent, than in the polar solvents such as Methyl Cellosolve, ethylene glycol, propanol and

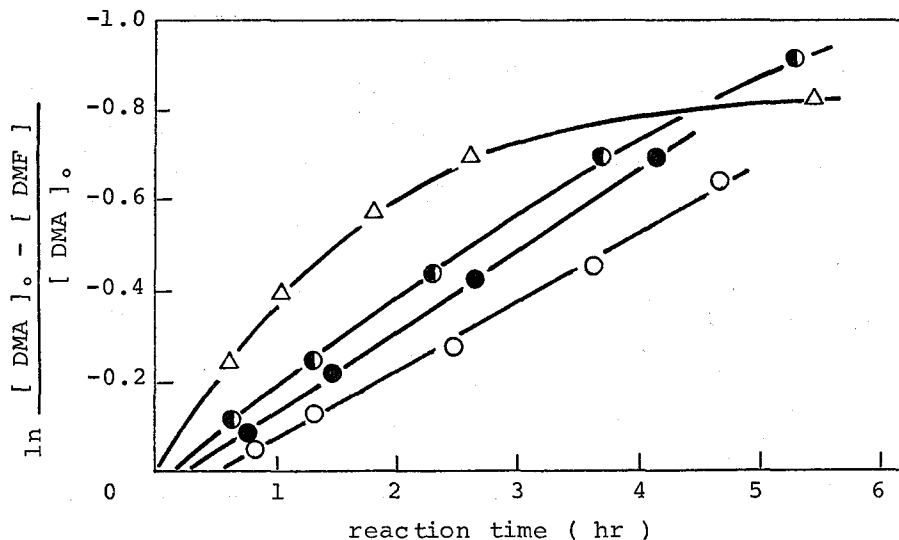


Fig. 3. Effect of volume ratio of MC and benzene in mixed solvent.

DMA=50 mmol, Cat=0.325 mmol, temp=105°C,  $P_{\text{CO}_2}$ =100 kg/cm<sup>2</sup>,  $P_{\text{H}_2}$ =100 kg/cm<sup>2</sup>, volume ratio of MC-benzene=○: (1/0), ●: (2/1), ◐: (1/2) and △: (0/1).

tetrahydrofuran (Table IV). The catalyst, however, lost its activity gradually during the reaction (Fig. 3) and this is conjectured to be mainly due to the reaction of  $\text{CO}_2$  with the catalyst to form an inactive species in benzene solution, which we did not intend to isolate (Table IV). In polar solvents other than tetrahydrofuran, such complication did not occur, but here an induction period was found to be quite long (140 min for ethylene glycol). This is the reason why we used the mixed solvent composed of MC and benzene. Mixture of MC and benzene in volume ratio 2:1 is the most suitable, *i.e.*, short induction period and absence of the deactivation of the catalyst (Fig. 3).

(c) *Catalyst concentration*: The over-all rate increases with the increase in the concentration of catalyst (Fig. 4). The plot of  $k_{\text{obs}}$  against concentration (Fig. 5) gives a nearly linear relation in the range of  $[\text{Cat}]_0 < 1.4 \times 10^{-4}$  (mole fraction). Thus, we can write the empirical expression (15), where  $A$  is a proportionality constant:

$$k_{\text{obs}} = A[\text{Cat}]_0 \quad (15)$$

When the catalyst concentration exceeds  $1.5 \times 10^{-4}$ , the larger deviation from the linearity is observed (Fig. 5). This can be explained as the result of some dimerization of the catalyst at high concentration. Because the dimer has been reported to be inactive in the case of hydrogenation of olefin,<sup>13)</sup> any dimer formed here can be thought to be inactive as catalyst.

(d) *Carbon dioxide and hydrogen pressure*: The effect of  $\text{CO}_2$  and  $\text{H}_2$  partial pressures was examined at two different temperatures (90°C and 105°C). The results are shown in Table IV. The rate at each temperature increases with the increase in the pressure of  $\text{CO}_2$  and  $\text{H}_2$ . The plot of the reciprocal of  $k_{\text{obs}}$  against the reciprocal pressure of  $\text{CO}_2$  or of  $\text{H}_2$  gives a straight line (Fig. 6). When the concentration of the



# High Pressure Synthesis of Dimethyl Formamide

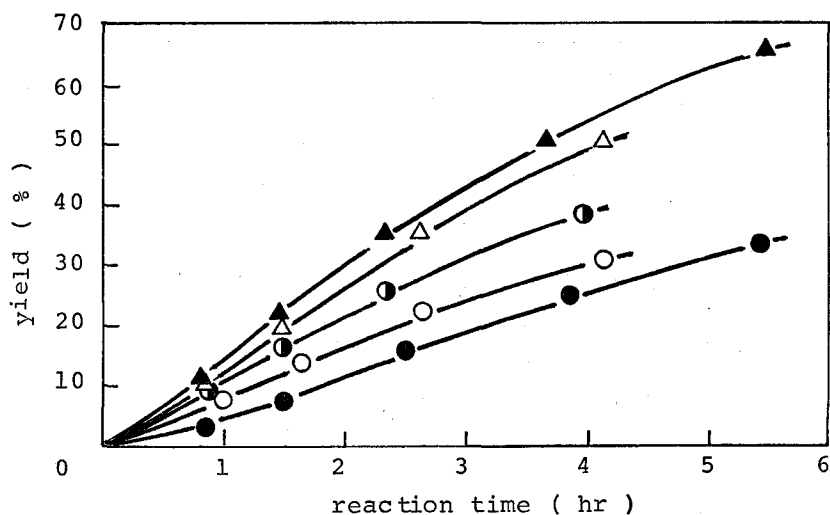


Fig. 4. Effect of catalyst concentration.

solvent: MC-benzene (2:1),  $[DMA]_0 = 0.0208$  mole fraction, temp = 105°C,  $P_{CO_2} = 100$  kg/cm<sup>2</sup>,  $P_{H_2} = 100$  kg/cm<sup>2</sup>,  $[Cat]_0 = \bullet$ :  $0.0468 \times 10^{-3}$  mole fraction,  $\circ$ :  $0.0705 \times 10^{-3}$  mole fraction,  $\odot$ :  $0.0941 \times 10^{-3}$  mole fraction,  $\triangle$ :  $140 \times 10^{-3}$  mole fraction,  $\blacktriangle$ :  $0.469 \times 10^{-3}$  mole fraction.

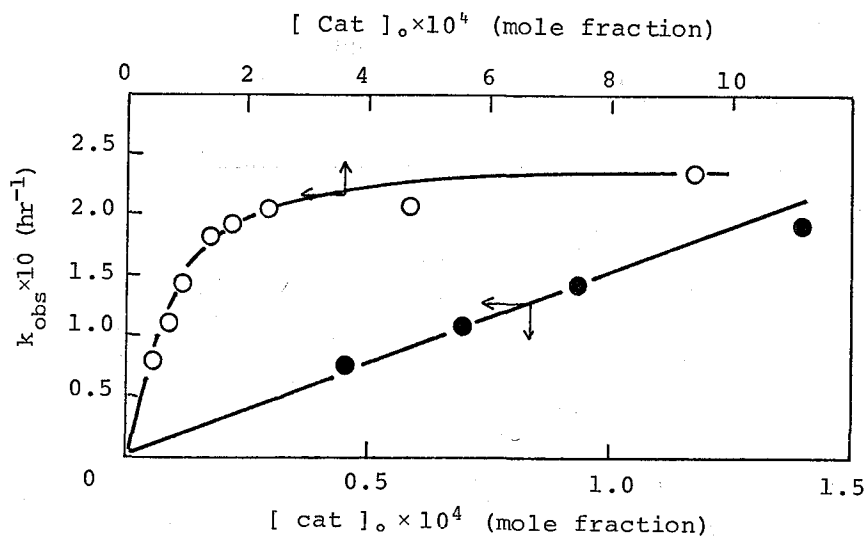


Fig. 5. Relation between  $k_{obs}$  and  $[Cat]_0$ .

Solvent: MC-benzene (2:1),  $[DMA]_0 = 0.0208$  mole fraction, temp = 105°C,  $P_{CO_2} = 100$  kg/cm<sup>2</sup>,  $P_{H_2} = 100$  kg/cm<sup>2</sup>.

gases dissolved in the mixed solvent is used instead of the pressure since Henry's law is obeyed,

$$\frac{1}{[CO_2]} = B \frac{1}{k_{obs}} + C, \quad (16)$$

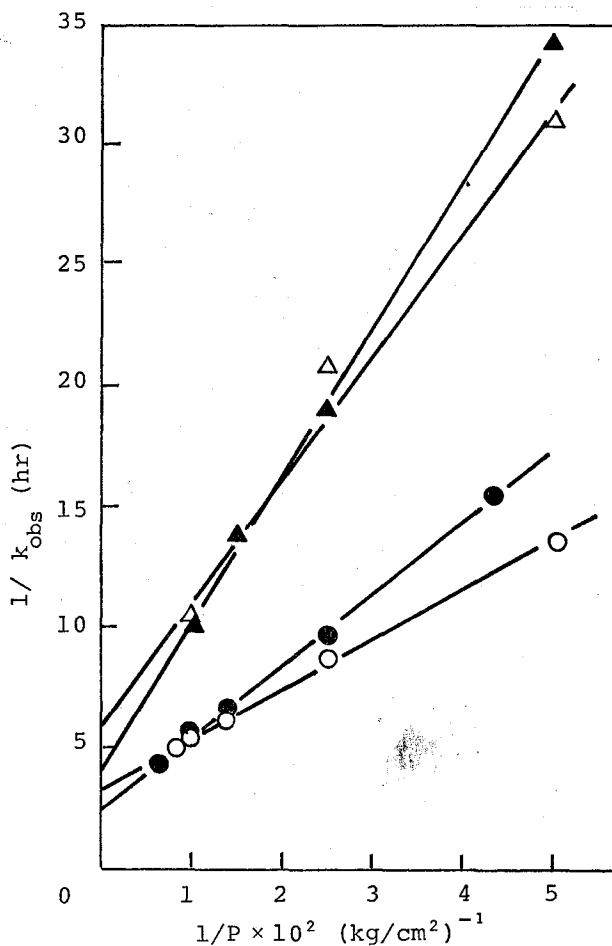


Fig. 6. Relation between  $1/k_{obs}$  and  $1/P$ .  
 solvent: MC-benzene (2:1),  $[DMA]_0 = 0.0208$  mole fraction,  
 $[Cat]_0 = 0.140 \times 10^{-3}$  mole fraction,  $P_{CO_2}$  effect:  $\circ$  ( $105^\circ C$ ),  $\bullet$  ( $90^\circ C$ ),  $P_{H_2} = 100$  kg/cm $^2$ ,  $P_{H_2}$  effect:  $\triangle$  ( $105^\circ C$ ),  $\blacktriangle$  ( $90^\circ C$ ),  $P_{CO_2} = 100$  kg/cm $^2$ .

$$\frac{1}{[H_2]} = D \frac{1}{k_{obs}} + E, \quad (17)$$

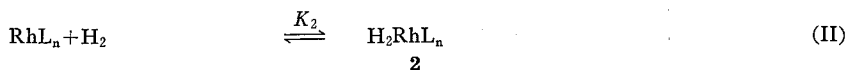
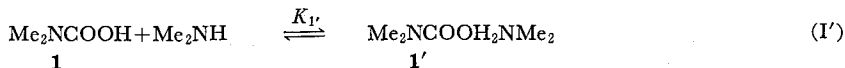
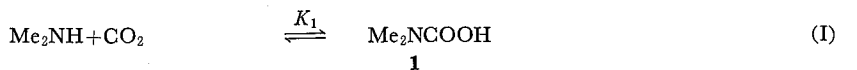
where  $B$ ,  $C$ ,  $D$  or  $E$  is a constant.

**Reaction mechanism.** Based on the above kinetic results, we will discuss the mechanism of the reaction. First, we are to assume that the reaction proceeds the courses as shown Scheme 1, where  $K_1$ ,  $K_1'$  and  $K_2$  represent the constants of the equilibrium and  $k_3$ ,  $k_{-3}$ ,  $k_4$ ,  $k_3'$ ,  $k_{-3}'$  and  $k_4'$  those of the rate of these steps.

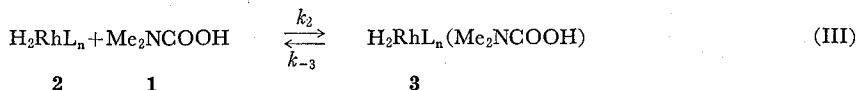
(a) **Reaction between  $CO_2$  and DMA:** It has been reported that  $CO_2$  reacts with amine to form carbamic acid **1** which further reacts with amine to form carbamate salt **1'**.<sup>12)</sup> These reactions are fast even at room temperature and low pressure,<sup>12)</sup> so the first step (I) and (I') of Scheme 1 should reach the equilibrium at the beginning of

# High Pressure Sythesis of Dimethyl Formamide

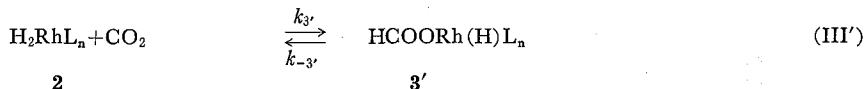
Scheme 1. Mechanism of the DMF formation reaction from DMA, CO<sub>2</sub> and H<sub>2</sub> with RhCl(PPh<sub>3</sub>)<sub>3</sub> as catalyst<sup>a)</sup>.



Carbamate Route.



Formate Route.



a) RhL<sub>n</sub> = RhCl(PPh<sub>3</sub>)<sub>2</sub>(HNMe<sub>2</sub>)

the reaction.

For the determination of  $K_1$  and  $K_{1'}$ , the concentration of CO<sub>2</sub> reacted with DMA ( $n$ ) was measured in the pressure range from 2 to 4 kg/cm<sup>2</sup>. The relation between  $n$  and the initial concentration of DMA( $a$ ) is plotted (Fig. 7). From Eqs. I and I' (Scheme 1), the concentration of **1** is given by Eq. (18),

$$[\mathbf{1}] = \frac{1}{2K_{1'}}(-1 + \sqrt{1 + 4K_1K_{1'}(a-n)c}), \quad (18)$$

where  $c$  represents the concentration of CO<sub>2</sub> in solution. If  $4K_1K_{1'}(a-n)c < 1$ , the following approximation will hold within the experimental limit:

$$\frac{n}{(a-n)c} \approx K_1 + K_1K_{1'}(a-n) \quad (19)$$

The plot of  $n/(a-n)c$  against  $(a-n)$  is shown in Fig. 8, from which the values of  $K_1$  and  $K_{1'}$  can be found (Table V), amounting to 220 as the average value of the product  $K_1K_{1'}$  at 105°C, thus our supposition,  $4K_1K_{1'}(a-n)c < 1$ , has been proved to be valid.

On the other hand, the product  $K_1K_{1'}$  is given as:

$$K_1K_{1'} = \frac{[\mathbf{1}']}{(a-n-[\mathbf{1}'])^2}. \quad (20)$$

Though the unstable carbamic acid has never been isolated, its existence in a large amount is conjectured from the inconstancy of the calculated values of  $K_1K_{1'}$  as seen in the right column of Table V, under the assumption that the quantity of **1** is negligibly

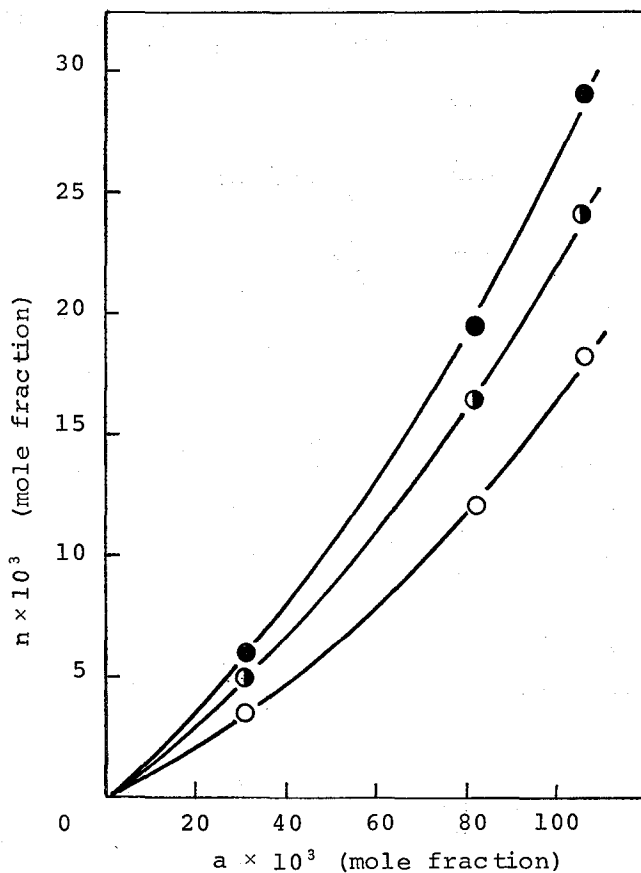


Fig. 7. Relation between initial concentration of DMA( $a$ ) and  $CO_2$  reacted with DMA ( $n$ ).

MC-benzene mixed solvent (2:1), temp=105°C, equilibrium pressure of  $CO_2$ =○: 2 kg/cm<sup>2</sup>, ◐: 3 kg/cm<sup>2</sup> and ●: 4 kg/cm<sup>2</sup>.

small, so that the product  $K_1K_1'$  is approximately equal to  $n/(a-2n)^2$ .

(b) *The hydride formation:* Tris(triphenylphosphine) rhodium(I) chloride liberates a molecule of triphenylphosphine to form a very reactive species  $RhCl(PPh_3)_2$  in organic solvent such as ethanol or benzene<sup>13)</sup> [Eq. (21)]. In the presence of a strong ligand like pyridine, this species reacts to give  $RhCl(PPh_3)_2(Py)$  which then forms a hydride complex  $H_2RhCl(PPh_3)_2(Py)$  with hydrogen.<sup>13)</sup> At room temperature,  $RhCl(PPh_3)_3$  dissolved rapidly in benzene solution of DMA and a dark yellow complex was obtained by recrystallization with hexane, which was identified as  $RhCl(PPh_3)_2(DMA)$  [Eq. (22)] from the elementary analysis (see the experimental). This complex must be the actual catalyst in the cycle of the amide formation, and is denoted by  $RhL_n$  in Scheme 1. From the kinetic results on the effect of the substrate concentration,  $RhCl(PPh_3)_3$  is thought to be almost transformed to  $RhL_n$  under the reaction conditions, *i. e.*,  $[RhL_n]_o = [RhCl(PPh_3)_3]_o$ . At 105°C, under the pressure of hydrogen,  $RhL_n$  reacts fast with hydrogen to form an amino-hydride complex  $H_2RhCl(PPh_3)_2(DMA)$ . Though we did not try to

# High Pressure Synthesis of Dimethyl Formamide

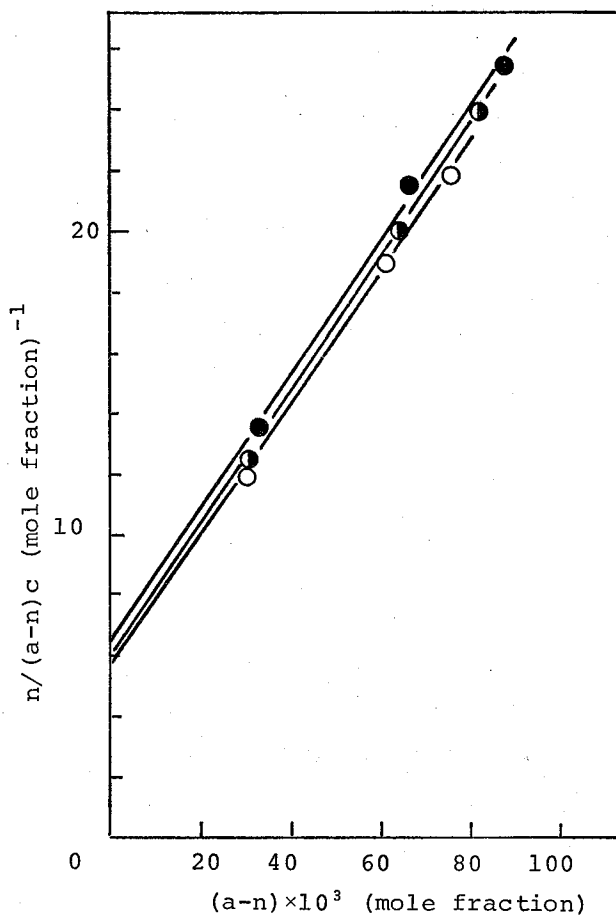


Fig. 8. Relation between  $a-n$  and  $n/(a-n)c$ .  
 MC-benzene mixed solvent (2: 1), temp=105°C,  $a$ =initial concentration of DMA,  $n$ =mole fraction of CO<sub>2</sub> reacted with DMA in liquid phase, equilibrium pressure of CO<sub>2</sub>=○: 2 kg/cm<sup>2</sup>, ◐: 3 kg/cm<sup>2</sup> and ●: 4 kg/cm<sup>2</sup>.

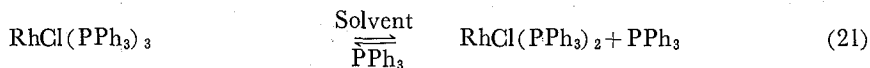
Table V. Equilibrium constants of the reaction between CO<sub>2</sub> and DMA at 105°C<sup>a)</sup>

$P_{CO_2}^e$ (kg/cm <sup>2</sup> )	$K_1$ (m.f.) <sup>-1</sup>	$K_1'$ (m.f.) <sup>-1</sup>	$K_1K_1'$ (m.f.) <sup>-2</sup>	$K_1K_1'^b$ (m.f.) <sup>-2</sup>		
				$a=0.105$	$a=0.0808$	$a=0.0356$
2	6.4	35	223	270	219	127
3	6.0	37	222	428	342	185
4	5.8	37	215	617	462	242
average	6.1	36	220			

a) Concentrations are expressed in mole fraction.

b) Calculated under the assumption that the quantity of Me<sub>2</sub>NCOOH<sub>2</sub>NMe<sub>2</sub> is negligibly small.

isolate this complex, its formation is quite probable because of the resemblance between pyridine and DMA as the ligands. This step must reach equilibrium within the induction period  $t_0$ . We neglect here any formation of dimers (for example  $\text{Rh}[\text{Cl}(\text{PPh}_3)_2]_2$  or  $[\text{H}_2\text{RhCl}(\text{PPh}_3)_2]_2$ ) in order to confine the discussion within the extent of low catalyst concentration ( $<1.5 \times 10^{-4}$ ).



(c) *The carbamate route and the formate route:* We will see later that from the rate equation, no clear distinction can be informed between the carbamate and the formate routes of Scheme 1. The evidence of the existence of the formate  $\text{HCOOML}_n$  has been proposed by the isolation of such complexes as  $\text{HCOORu}(\text{H})(\text{PPh}_3)_4$ ,<sup>7)</sup>  $\text{HCOOCo}(\text{PPh}_3)_4$ ,<sup>14)</sup> and  $\text{H}_2\text{Rh}(\text{OOCH})(\text{PR}_3)_2$ .<sup>21)</sup> Since the two first formates give easily methyl formate with methyl iodide,<sup>7,14)</sup> it is quite possible that, also in our case,  $\text{CO}_2$  could react with  $\text{H}_2\text{RhL}_n$  to form similar formate which would subsequently react with DMA to form DMF (formate route). However, from the following several experiments, no evidence of such insertion has been found. After the catalyst was heated for 3 h in the mixed solvent under 100 kg/cm<sup>2</sup> of  $\text{CO}_2$  and 100 kg/cm<sup>2</sup> of  $\text{H}_2$  at 105°C, this solution was treated with methyl iodide to give no trace of methyl formate. We reexamined this in the medium basified by tributylamine which does not react with  $\text{CO}_2$ ,<sup>15)</sup> but, here too, methyl formate has never been detected at the same treatment as above. Moreover, even is the reaction carried out in methanol solvent, no trace of methyl formate been found during the reaction, even in the induction period. These results may contradict to that of Hirai *et al.*,<sup>16)</sup> who reported the synthesis of  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$  from  $\text{RhCl}(\text{PPh}_3)_3$ ,  $\text{CO}_2$  and  $\text{H}_2$  and explained its formation as the result of the reaction between the formic acid formed from  $\text{HCOORh}(\text{H})(\text{PPh}_3)_2$ , and  $\text{RhCl}(\text{PPh}_3)_2$ . But this kind of carbonyl complex should be inactive toward our amide formation since the presence of a small amount of carbon monoxide was found to prevent the reaction completely probably by transforming the catalyst to the carbonyl species.<sup>17)</sup> This fact seems to contradict to the results of Saegusa *et al.* who prepared amide from amine and carbon monoxide with copper complex catalyst,<sup>18)</sup> or those of Stern *et al.* who used  $\text{PdCl}_2$  as catalyst for the preparation of isocyanate from amine and carbon monoxide.<sup>19)</sup> The mechanism of these reactions has not been made clear, but the possibility that a carbonyl complex should be an intermediate for the carbonylation of amine under the presence of carbon monoxide can be eliminated in our present studies carried out in the absence of carbon monoxide. Thus we deny the formation of carbonyl species and its precursor, the formate complex. As there may arise an objection that if the amount of the formate formed were too small to be detected, its existence could not be denied from the above results, an examination on the induction period was carried out. After stirring the solution of the catalyst under  $\text{CO}_2$  and  $\text{H}_2$  pressure for about 30 min, the substrate was added to this solution to start the reaction at this moment (Fig. 9). Perhaps 30 min is long enough for  $\text{HCOORh}(\text{H})\text{L}_n$  to reach its equilibrium concentration, so that

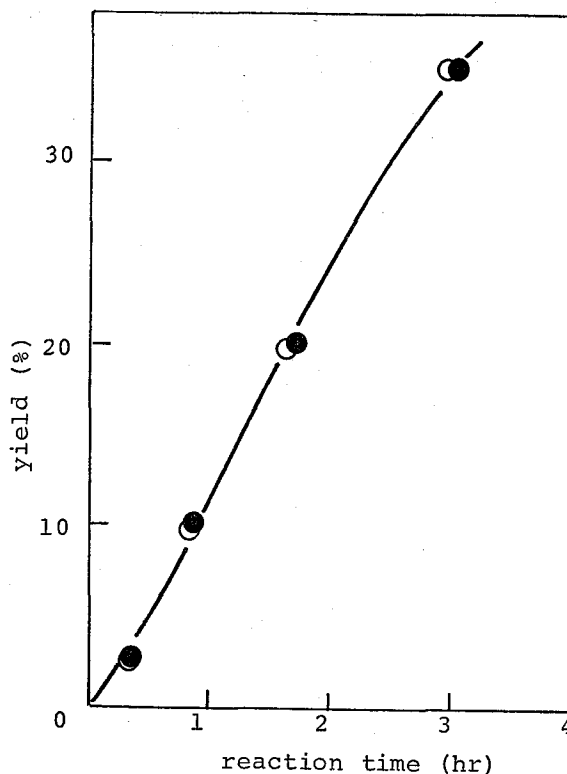
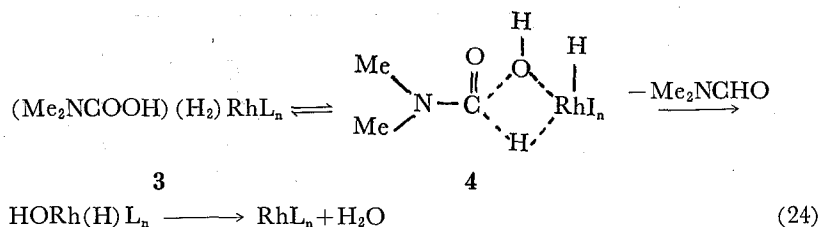


Fig. 9. Effect of the charging order of DMA on the induction period. solvent: MC-benzene (2: 1),  $[\text{DMA}]_0 = 0.0208$  mole fraction, temp =  $105^\circ\text{C}$ ,  $P_{\text{CO}_2} = 100 \text{ kg/cm}^2$ ,  $P_{\text{H}_2} = 100 \text{ kg/cm}^2$ . ○: reaction carried out in ordinary way (see text), ●: DMA was added after stirring the solution for 30 min.

in this way disappearance of the induction period should be expected if the formate really had formed. No disappearance of the induction period as shown in Fig. 9 is a strong evidence against the formation of  $\text{HCOORh}(\text{H})\text{L}_n$ . The only rhodium formate  $\text{H}_2\text{Rh}(\text{COOH})(\text{PR}_3)_2$  prepared by Otsuka *et al.*<sup>21)</sup> has been reported to react with carbon dioxide to form a carbonyl complex. This rhodium formate seems to be inactive to pyridine, the amine used as solvent.<sup>21)</sup> This is also another important fact to support our conclusion because the formate complex will be inactive toward an amine even if it has formed.

We shall now consider another path, that is, the formation of the carbamate complex 3. Extine *et al.*<sup>20)</sup> have proposed in the case of tungsten or vanadium that the formation of similar carbamates occurred due to the substitution of amine ligands by the carbamic acid 1 and that the carbamate salt 1' was inactive. We would, however, assume here the formation of 7-coordination intermediate 3 by step (III), which may be unstable and decompose to give DMF, water and the catalyst  $\text{RhL}_n$  [Eq. (24)]. We proposed here an intermediate 4 which results from the attack of the hydrogen atom of the rhodium hydride complex on the carbon of the carbonyl group [Eq. (24)].



*Rate equation.* From the above mentioned assumption, the rate equation of the producing DMF will be derived. The concentration of 1 can be obtained as:

$$[1] = \frac{1 + K_1[\text{CO}_2]}{4K_1'} \left\{ -1 + \sqrt{1 + \frac{8K_1K_1'([\text{DMA}]_0 - [\text{DMF}])[\text{CO}_2]}{(1 + K_1[\text{CO}_2])^2}} \right\} \quad (25)$$

With the present reaction conditions and the measured values of  $K_1$  and  $K_1'$  (Table V), the second term in the root of Eq. (25) is inferred to be smaller than unity so that the following approximate expression can be obtained within the error of 6%:

$$[1] \doteq \frac{K_1([\text{DMA}]_0 - [\text{DMF}])[\text{CO}_2]}{1 + K_1[\text{CO}_2]} \quad (26)$$

This approximation means that under high pressure of  $\text{CO}_2$ , the quantity of the carbamate salt 1' is negligibly small compared to that of the carbamic acid. The application of steady state approximation to 3 gives the integral from of the rate equation as:

$$\ln \frac{[\text{DMA}]_0 - [\text{DMF}]}{[\text{DMA}]_0} = - \frac{k_3k_4K_1K_2[\text{CO}_2][\text{H}_2][\text{Cat}]_0}{(k_{-3} + k_4)(1 + K_1[\text{CO}_2])(1 + K_2[\text{H}_2])} \quad (27)$$

This agrees with the empirical equation (14), and the observed rate constant  $k_{obs}$  can be written as below:

$$k_{obs} = \frac{k_3k_4K_1K_2[\text{CO}_2][\text{H}_2][\text{Cat}]_0}{(k_{-3} + k_4)(1 + K_1[\text{CO}_2])(1 + K_2[\text{H}_2])} \quad (28)$$

Thus, its inverse can be expressed as:

$$\frac{1}{k_{obs}} = \frac{(k_{-3} + k_4)(1 + K_2[\text{H}_2])}{k_3k_4K_1K_2[\text{H}_2][\text{Cat}]_0} \cdot \frac{1}{[\text{CO}_2]} + \frac{(k_{-3} + k_4)(1 + K_2[\text{H}_2])}{k_3k_4K_2[\text{H}_2][\text{Cat}]_0}, \quad (29)$$

or

$$\frac{1}{k_{obs}} = \frac{(k_{-3} + k_4)(1 + K_1[\text{CO}_2])}{k_3k_4K_1K_2[\text{CO}_2][\text{Cat}]_0} \cdot \frac{1}{[\text{H}_2]} + \frac{(k_{-3} + k_4)(1 + K_1[\text{CO}_2])}{k_3k_4K_1[\text{CO}_2][\text{Cat}]_0} \quad (30)$$

Eqs. (28), (29) and (30) agree with the empirical Eqs. (15), (16) and (17), and from the experimental values of  $B$ ,  $C$ ,  $D$  and  $E$  (Fig. 6), equilibrium and rate constants can be calculated as seen in Table VI.

Table VI. Values of observed constants in Scheme 1

temp (°C)	$K_1$ (m. f.) <sup>-1</sup>	$K_2$ (m. f.) <sup>-1</sup>	$\frac{k_3k_4}{k_{-3} + k_4}$
90	2.6	19	$2.8 \times 10^3$
105	3.6	20	$4.5 \times 10^3$



Thus, the carbamate route mechanism proposed in Scheme 1 is the reasonable one that satisfies our experimental results. In addition, the good agreement in the order of magnitude between both values of  $K_1$  from the kinetics (3.6, Table VI) and direct measurement (6.1, Table V) should be another evidence for this mechanism. Unfortunately, the rate constant of the rate-determining step (III),  $k_3$ , cannot be derived here as an independent value.

The temperature coefficient of  $k_{obs}$  is obtained as 13 kcal/mol from the Arrhenius' plot as shown in Fig. 10. From Eq. (31), the following relation is obtained approximately:

$$-\frac{d \ln(k_{obs})}{Rd(1/T)} = -\frac{d \ln K_1}{Rd(1/T)} - \frac{d \ln K_2}{Rd(1/T)} - \frac{d \ln \{k_3 k_4 / (k_{-3} + k_4)\}}{Rd(1/T)} \quad (31)$$

From the two values of  $K_1$  and  $K_2$  at 90°C and 105°C (Table VI), the heat of formation

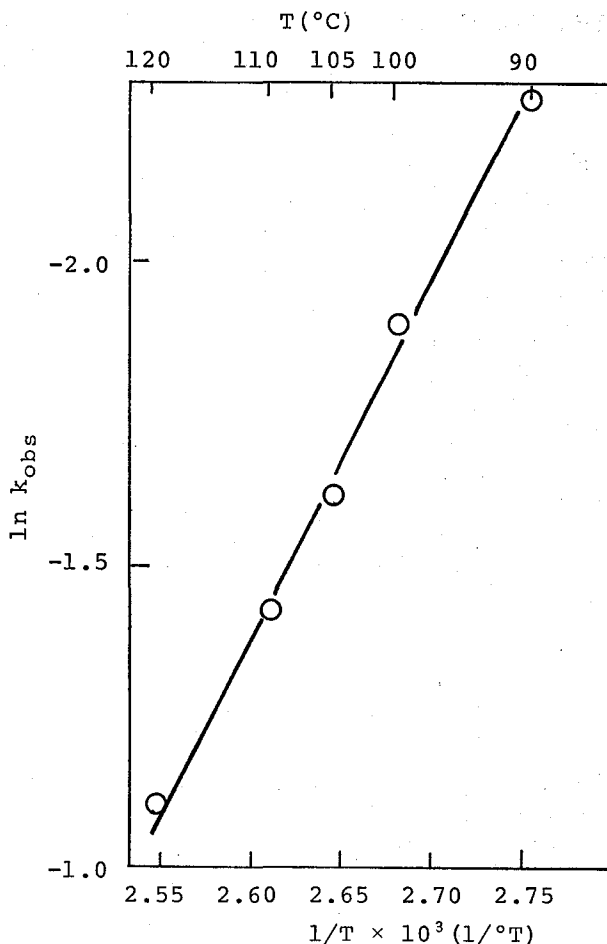


Fig. 10. Arrhenius plot of  $k_{obs}$ .  
 solvent: MC-benzene (2:1), DMA=50 mmol, Cat=0.542 mmol,  
 $P_{CO_2}$ =100 kg/cm<sup>2</sup>,  $P_{H_2}$ =100 kg/cm<sup>2</sup>.

of reaction (I) is found to be 5.9 kcal/mol and that of reaction (II) 0.9 kcal/mol. Eq. (31) gives then 7 kcal/mol as the value of  $(1/R) \ln \{k_3 k_4 / (k_{-3} + k_4)\} / d(1/T)$ . As  $k_4$  and  $(k_{-3} + k_4)$  was supposed to be much greater than  $k_3$ , this value 7 kcal/mol can be thought to be the activation energy of the rate-determining step (III).

Finally the rate equation for the mechanism involving the formate route is derived as:

$$\frac{d[\text{DMF}]}{dt} = \frac{k_3' k_4 K_2 [\text{CO}_2] [\text{H}_2] [\text{Cat}]_0 ([\text{DMA}]_0 - [\text{DMF}])}{(1 + K_1 [\text{CO}_2]) (1 + K_2 [\text{H}_2])} \quad (32)$$

As this rate equation also agrees with the empirical Eqs. (15), (16) and (17), it should be emphasized as discussed above, not solely from the kinetic results, that we denied this formate route.

## EXPERIMENTAL

*Materials.* Tris(triphenylphosphine)rhodium(I) chloride was obtained from the Stem Chemicals Inc., and used without further purification. All the solvents were distilled by the usual method. The other substances such as dimethylamine, N,N-dimethylformamide and mesitylene were used without further purification. Hydrogen and carbon dioxide were materials with a purity of higher than 99%. Hydrogen was compressed by a compressor, while the liquefied carbon dioxide was first introduced at 0°C in an autoclave to an amount so that a desired pressure (200 to 400 kg/cm<sup>2</sup>) was obtained when heated at 100°C.

*Procedure of the kinetic measurement.* Reactions were carried out in a stainless-steel autoclave (cal. 234 ml) equipped with a magnetic stirrer and a sampling line (it was confirmed that the wall of the autoclave in contact with the solution did not affect the reaction). Tris(triphenylphosphine)rhodium(I) chloride (0.1 to 1 mmol), a solution of dimethylamine in the mixed solvent (the total volume 100 ml) and mesitylene (0.8 ml) were placed in the autoclave, which was heated up to 90 to 130°C within 60 min and maintained over 30 min at the reaction temperature. Then, hydrogen was charged up to the desired pressure (20 to 160 kg/cm<sup>2</sup>) and the stirring was started (1200 rpm). After the hydrogen was completely dissolved (within 1 min), carbon dioxide was added up to the desired pressure (120 to 260 kg/cm<sup>2</sup>) and this time was taken as the beginning of the reaction ( $t=0$ ). Carbon dioxide dissolved completely within 2 min. The stirring was stopped from time to time and a sample of about 1 ml was taken out through the sample into a trap, while in order to keep the pressure constant during the reaction carbon dioxide was supplied from the reservoir.

*Analysis.* Dimethylamine and N,N-dimethylformamide were determined quantitatively by gas chromatography with mesitylene as an internal standard (Yanagimoto GCG 550F, polyethylene glycol column (2m, 3mm  $\phi$ ) with nitrogen carrier at 120°C).

*Solubility of gases.* An amount of a solution containing the dissolved gas was withdrawn through the sampling line and the volume of released gas trapped in a gas-burette (cal 500 ml) was measured at 1 atm. The solubility of the gases in the reaction medium was presumed to be equal to that in the solution without the catalyst and the substrate.

## High Pressure Synthesis of Dimethyl Formamide

*Reaction of carbon dioxide and dimethylamine.* 200 ml of a solution of dimethylamine (0.0356 to 0.105 mole fraction) was put in the autoclave and heated up to 105°C. From the storage (cal 50 ml) carbon dioxide was added and its quantity absorbed at any equilibrated pressure (1 to 4 kg/cm<sup>2</sup>) was obtained from the pressure drop of reservoir read from a gauge. The difference between this amount and that of carbon dioxide physically absorbed in the mixed solvent as measured in the same way, was assumed to be equal to the amount which reacted with the amine.

*Preparation of  $\text{RhCl}(\text{PPh}_3)_2(\text{HNMe}_2)$ .* 0.5 g of  $\text{RhCl}(\text{PPh}_3)_3$  dissolved rapidly in a solution of dimethylamine (8.4 mmol) in 20 ml of benzene at room temperature. The product was precipitated by the addition of 50 ml of hexane, collected and washed with ether and dried *in vacuo*: yield, 0.34 g (67%), elementary analysis (found: C=60.20%, H=5.04%, N=1.59%;  $\text{RhCl}(\text{PPh}_3)_2(\text{HNMe}_2)$  requires C=64.50%, H=5.10%, N=1.98%).

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